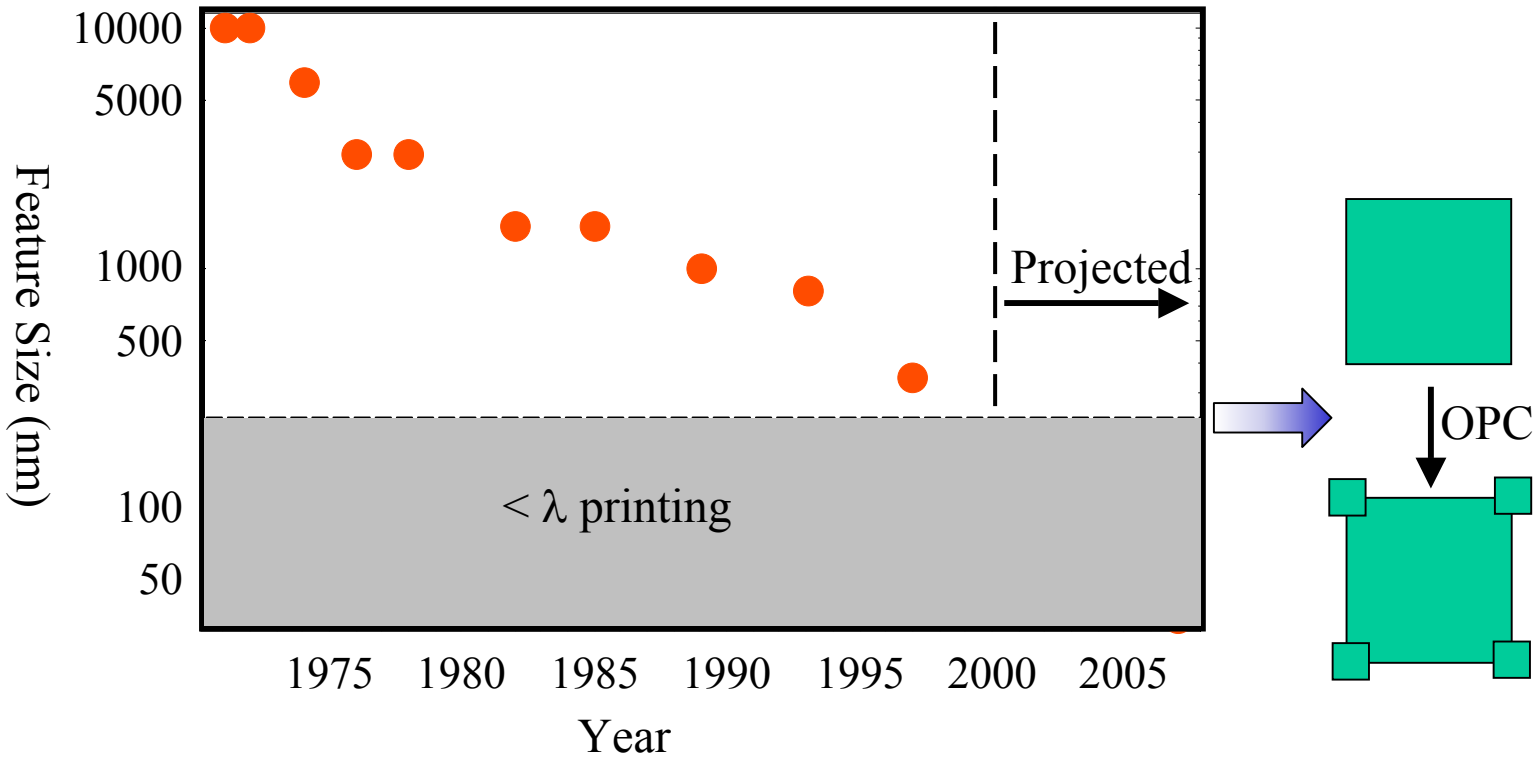
Resist Materials I

- Resist Basics
  - Sensitivity
  - Contrast
  - Coating and Film Formation
- Resist Requirements
  - Process Stability
  - Contrast
  - Sensitivity
  - Etch Resistance
  - Resolution

Introduction to Microlithography, L.F. Thompson, C.G. Willson and M.J. Bowden, ACS Professional Reference Book (1994)

Demands on E-beam Systems

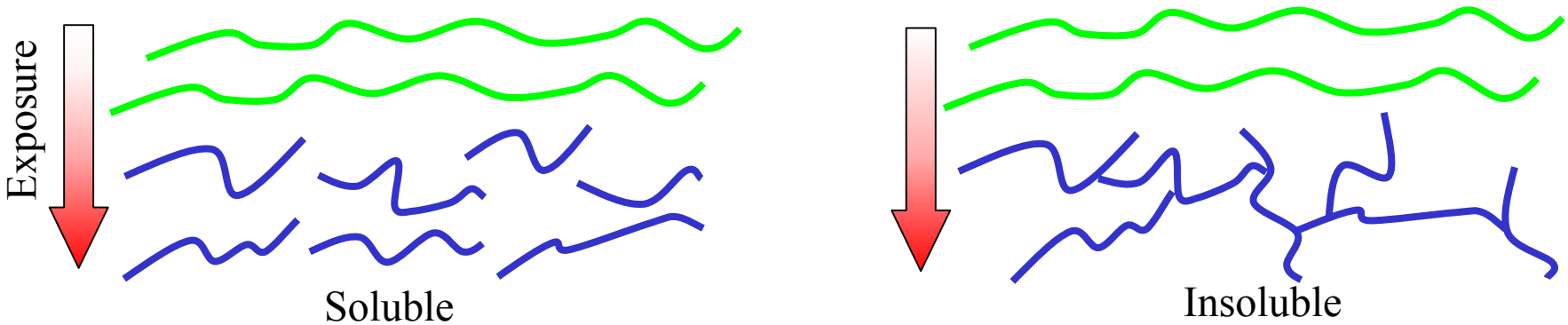


- Introduction of RET ➢ mask features ≈1x
- Reduction in feature size ➢ projection e-beam
  - Sensitivity *and* Resolution *and* Process Robustness needed

Data: Intel Corp./ITRS

Effect of Radiation on Polymers

- Two competing effects: main chain scission (s) and cross-linking (x)
  - If scission dominates then the polymer chains become shorter and more soluble (positive tone)
  - If cross-linking dominates then the polymer chains form a three-dimensional network and become insoluble (negative tone)



Quantifying Response to Radiation

$$\text{Number average molecular weight}: \quad M_n^0 = \frac{wN_A}{N_0} \quad \Rightarrow \quad N_0 = \frac{wN_A}{M_n^0}$$

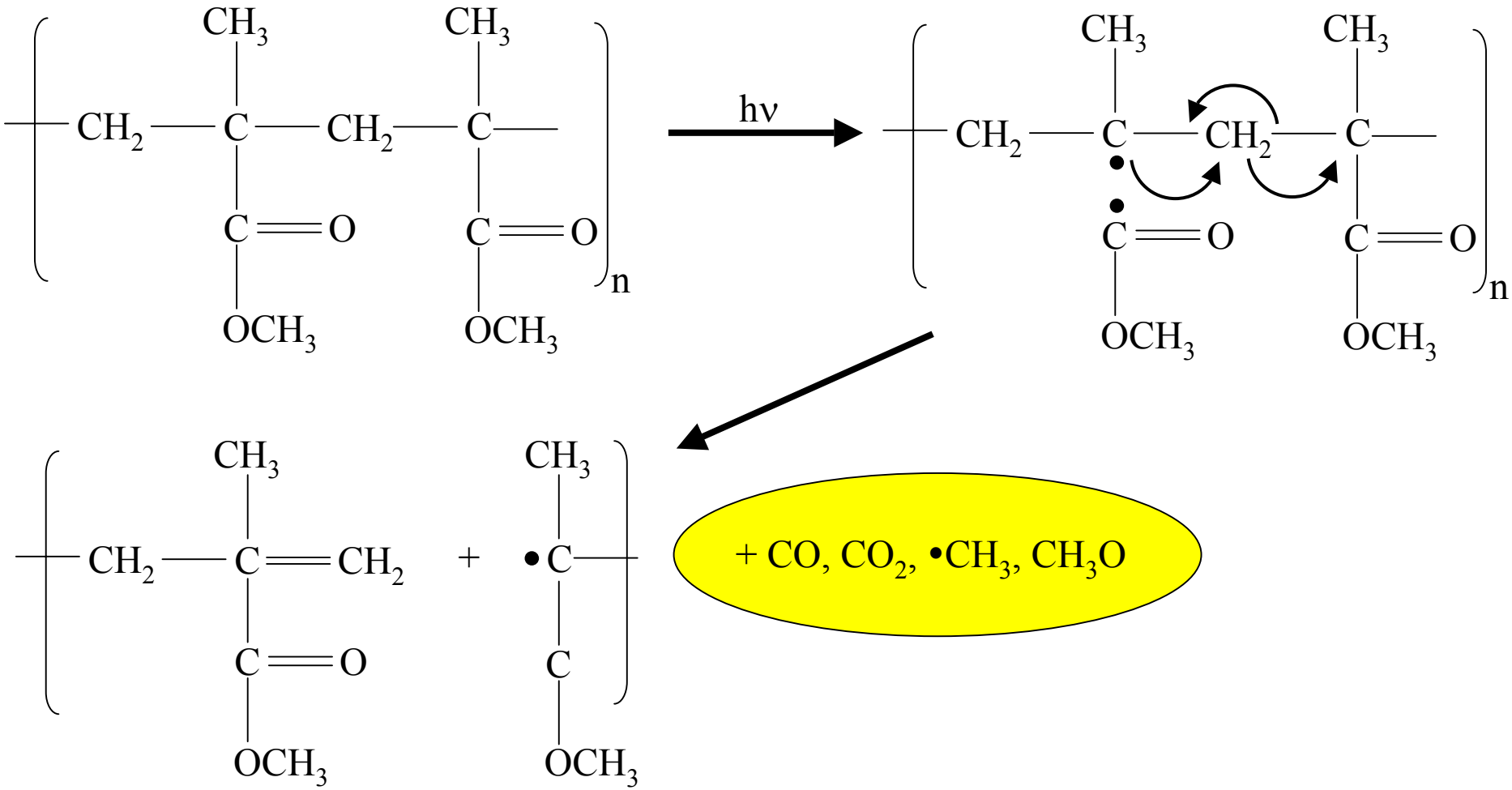
$$w = \text{sample weight}(g),\ N_A = \text{Avogadro's Number},\ N_0 = \text{Number of Molecules}$$

$$\text{Absorbed dose} = D\,(ev/g),\ \text{Number of Scissions} = N^*[G(s)/100]Dw$$

$$M_n^* = \frac{wN_A}{N_0 + N^*} \quad \Rightarrow \quad \frac{1}{M_n^*} = \frac{1}{M_n^0} + [G(s)/100N_A]D$$

- *G(s)*, *G(x)* = number of scissions, x-links/100 eV of deposited energy
  - *G(s)* values range from 1.3 (PMMA) to 10 (poly(olefin sulfones))
  - *G(x)* values range from 0.1 (poly(ethene)) to 10 (epoxy-side chains)

PMMA - Positive Resist



HSQ - Negative Resist

$HOSiO_{3/2} + SiO_2 + H_2\uparrow + H_2O\uparrow$

Hydrolysis,
H_2O

$HSiO_{3/2}$
Cage-Like
Structure

Bond
Rearrangement,
300-500 °C

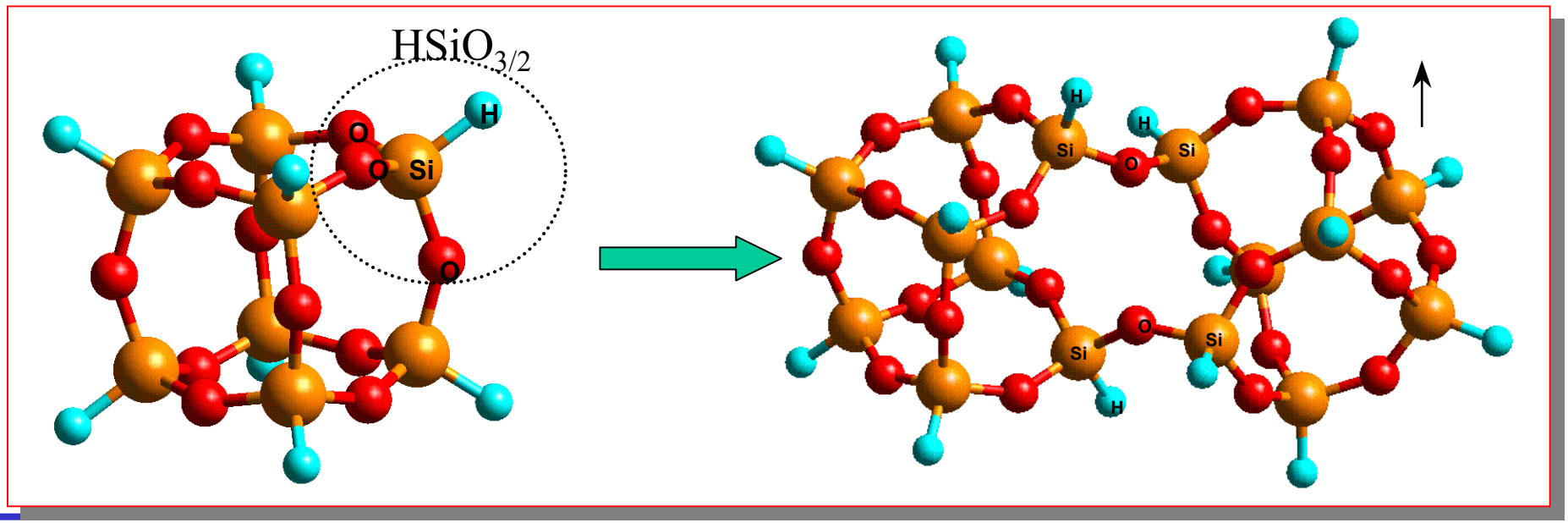
$HSiO_{3/2}$
Network Structure

Oxidation,
>350 °C, $[O_2]$ > 50 ppm

Redistribution,
400-550 °C

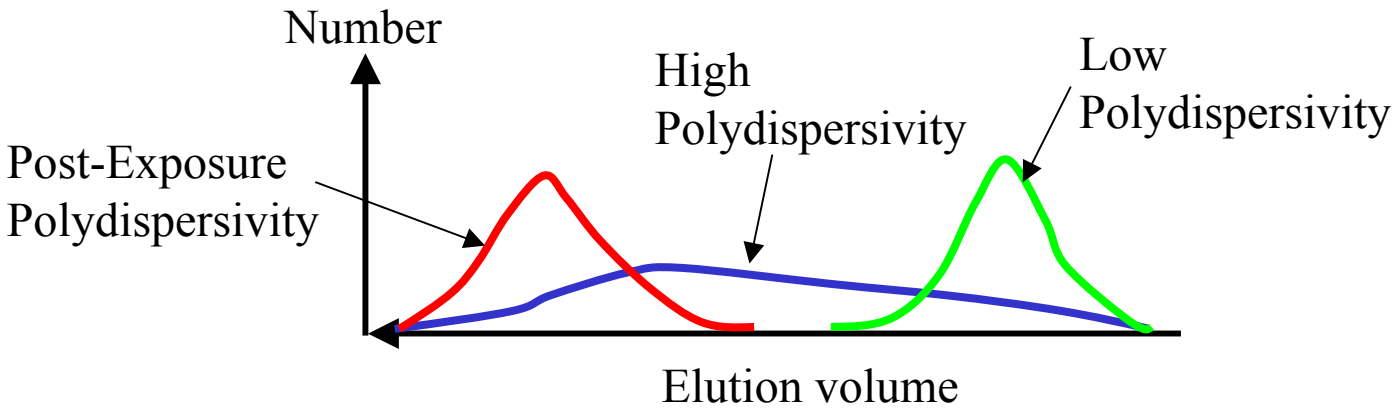
$HOSiO_{3/2} + SiO_2 + H_2\uparrow + H_2O\uparrow$

$SiO_2 + SiH_4$



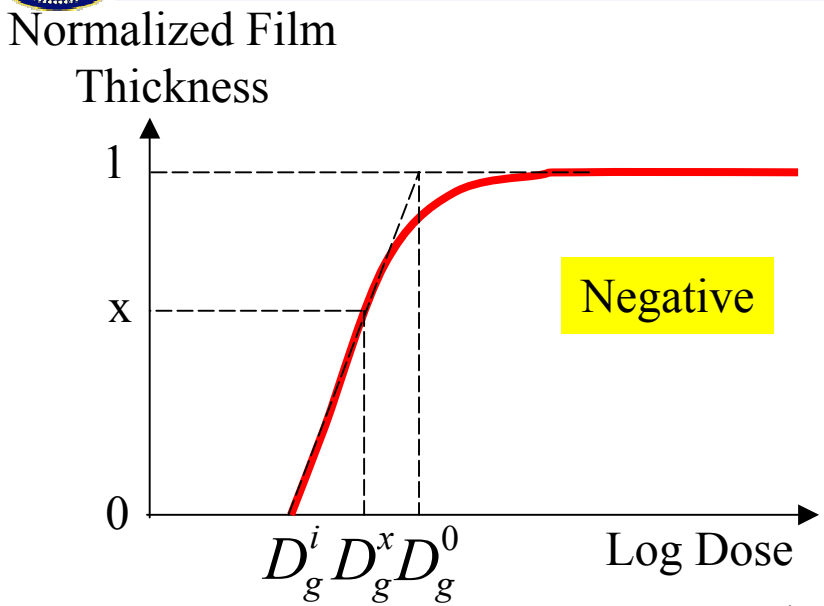
Contrast Mechanism in Single Component Resist

- Single component materials (e.g. PMMA) ➢ main-chain scissioning leads to reduction in molecular weight
  - Developer removes low molecular weight material first
  - Need large difference in pre- and post-exposure molecular weights (100 x)
    - ➢ High molecular weight starting material
  - Low contrast mechanism, but can be optimized by minimizing polydispersivity (M_w/M_n)

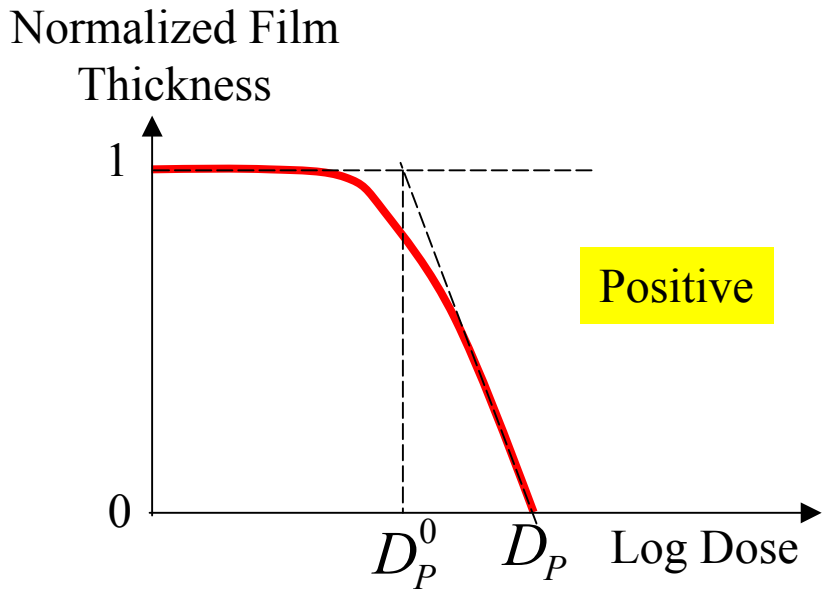


After M.J. Bowden, L.F. Thompson and J.P. Ballantyne, J. Vac. Sci. Technol., **12**, 1294 (1975)

Contrast



$$Contrast : \gamma_n = \left[\log \frac{D_g^0}{D_g^i} \right]^{-1}$$



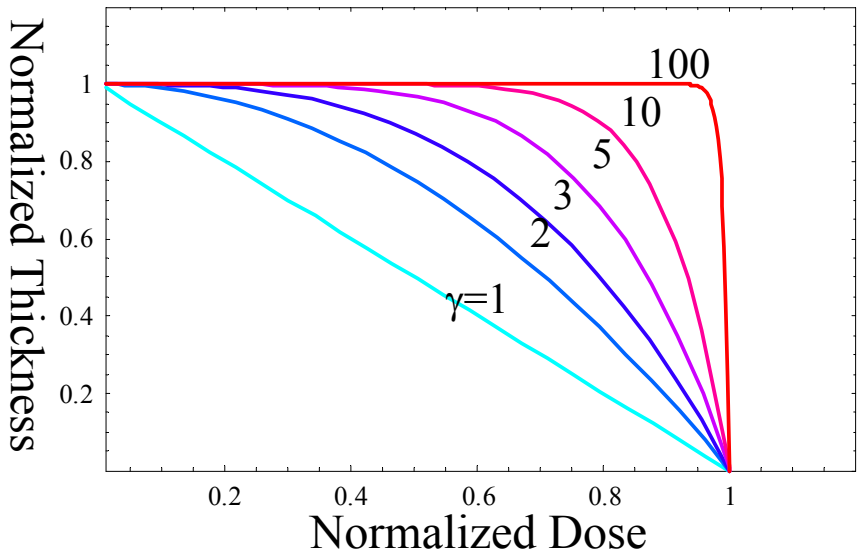
$$Contrast : \gamma_p = \left[\log \frac{D_P}{D_P^0} \right]^{-1}$$

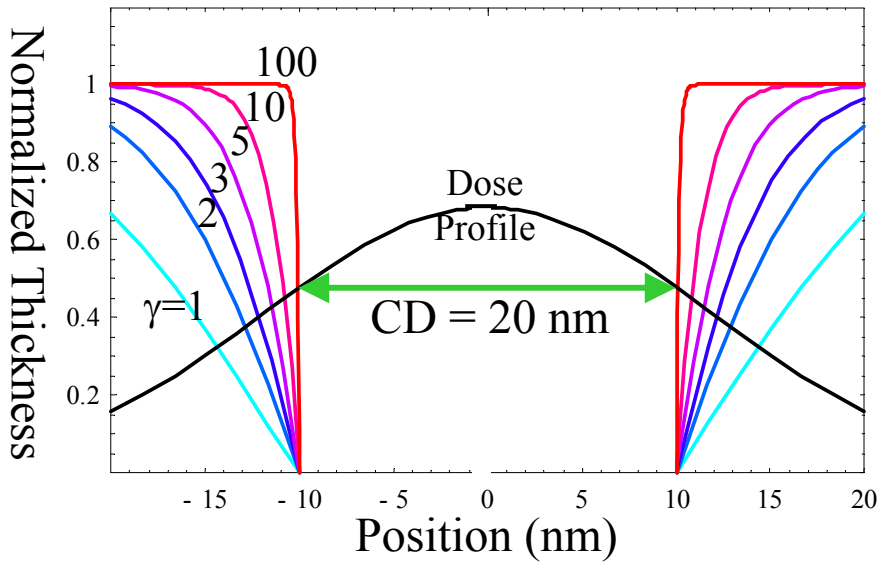
- High contrast is essential to achieving high resolution. Low contrast is useful in forming surface topography.

Contrast

Dissolution rate contrast: $\gamma = \dfrac{d \ln r}{d \ln E}$

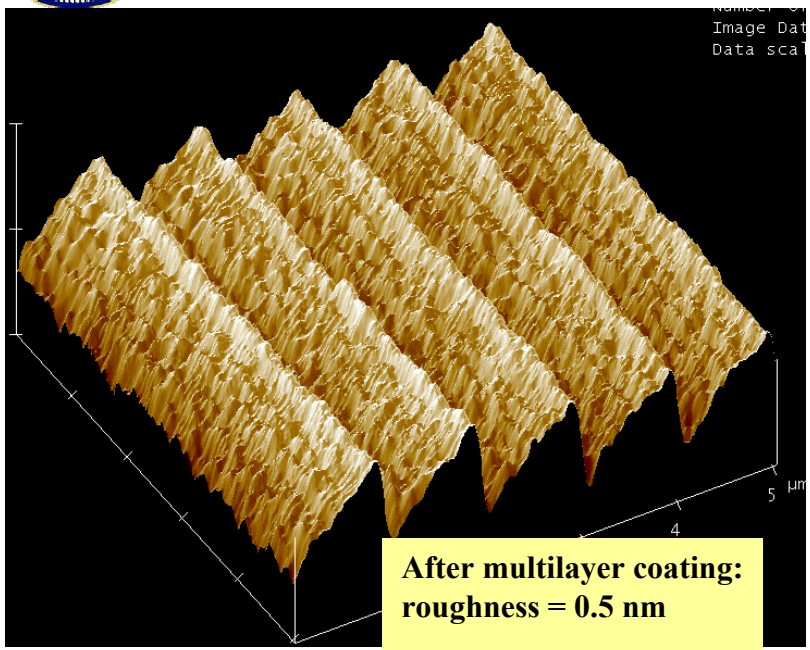
$$PSF = \frac{e^{-(x-x_0)^2/2\sigma^2}}{\sigma\sqrt{2\pi}}, \sigma = 10\ nm$$



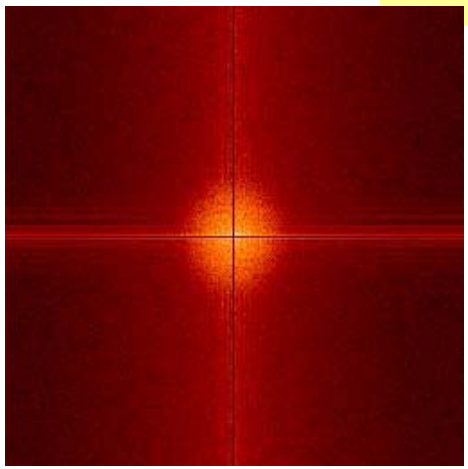


- Contrast affects:
  - Resolution
  - Development stability
  - Etch resistance (remaining thickness)
- Required value > 5

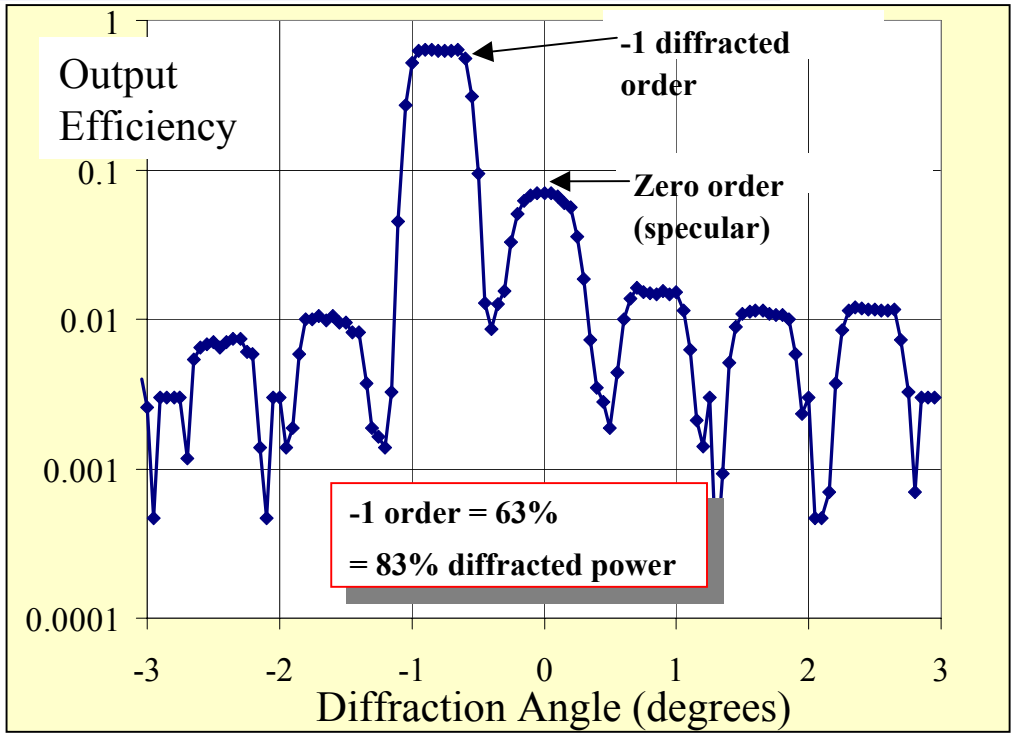
Spectral Purity Filter Performance

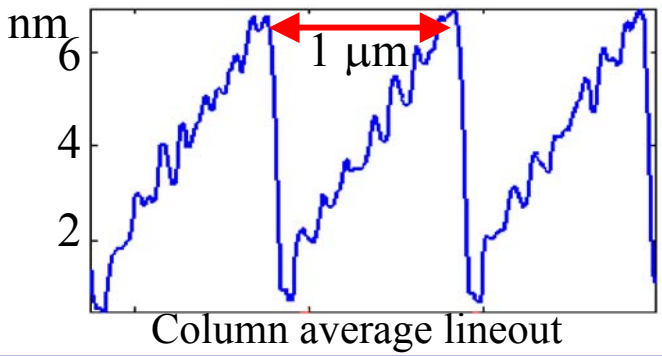


After multilayer coating: roughness = 0.5 nm



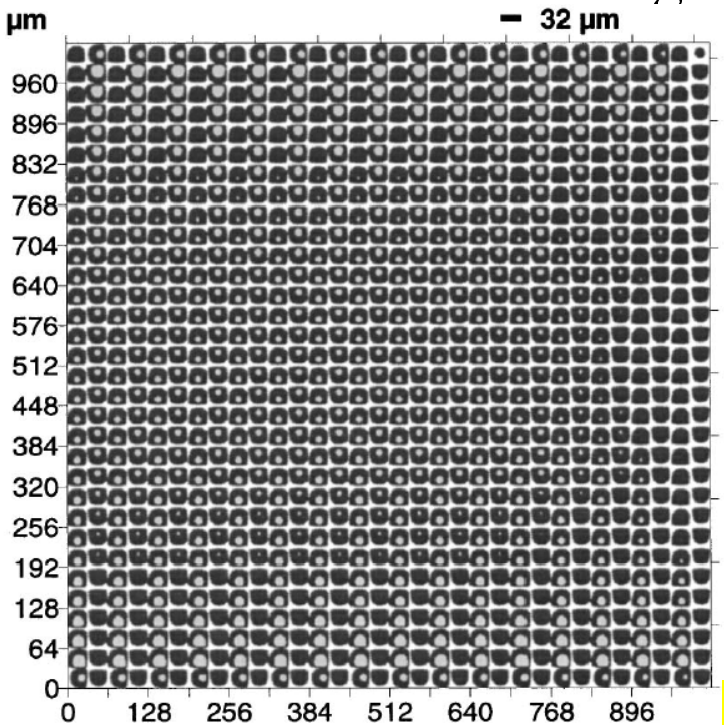
Light is scattered by surface roughness – loss in diffracted power
⇐ PSD of multilayer coated grating

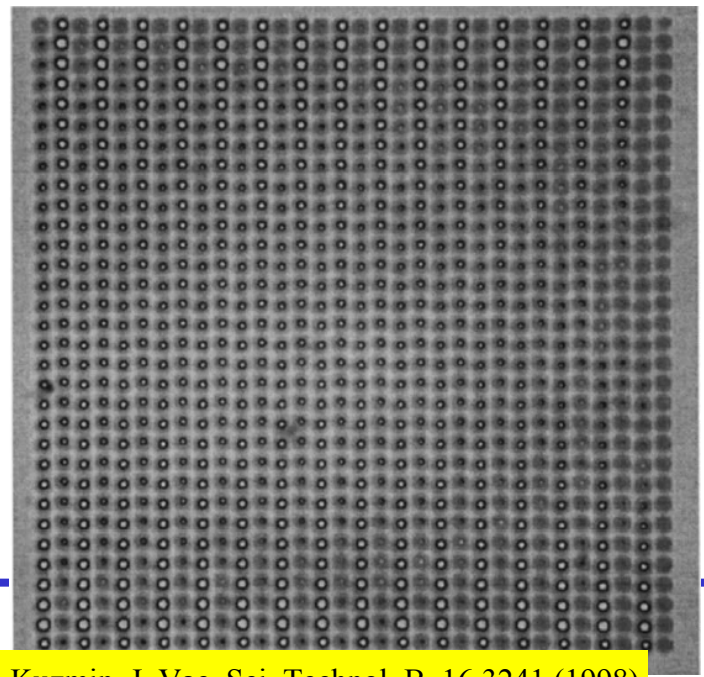




Sensitivity

- Sensitivity improved by making each electron do more chemistry
  - Reduces demands on source (key driver in optical lithography) ➢ increased throughput
  - Reduces space charge
  - Reduces wafer heating ➢ improved pattern placement

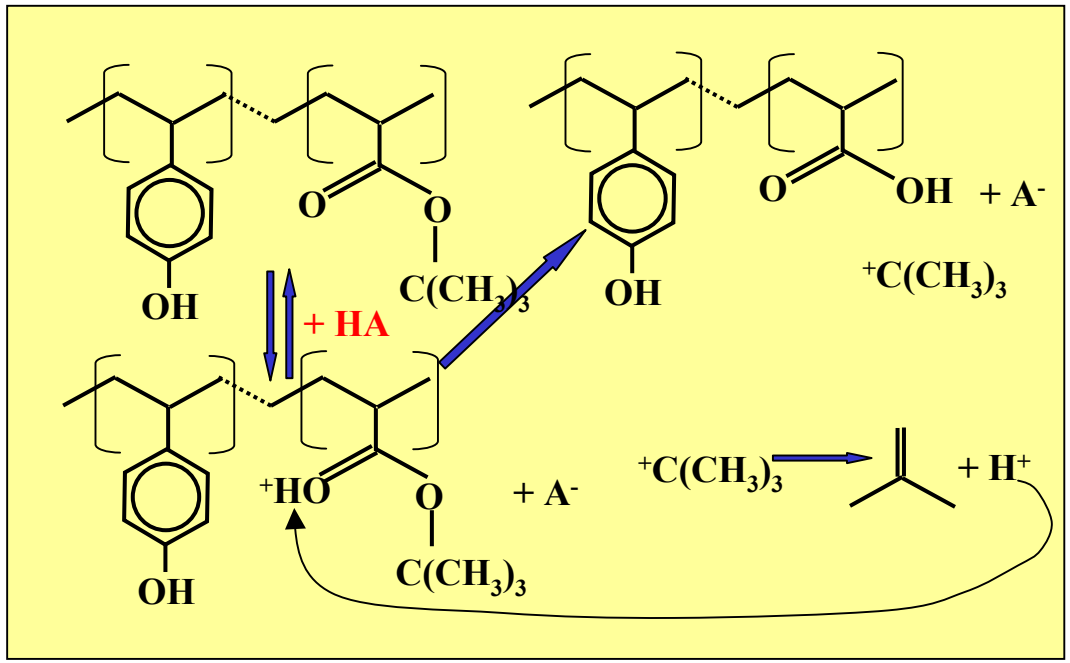




S. Babin, I. Kuzmin, J. Vac. Sci. Technol. B, 16 3241 (1998)

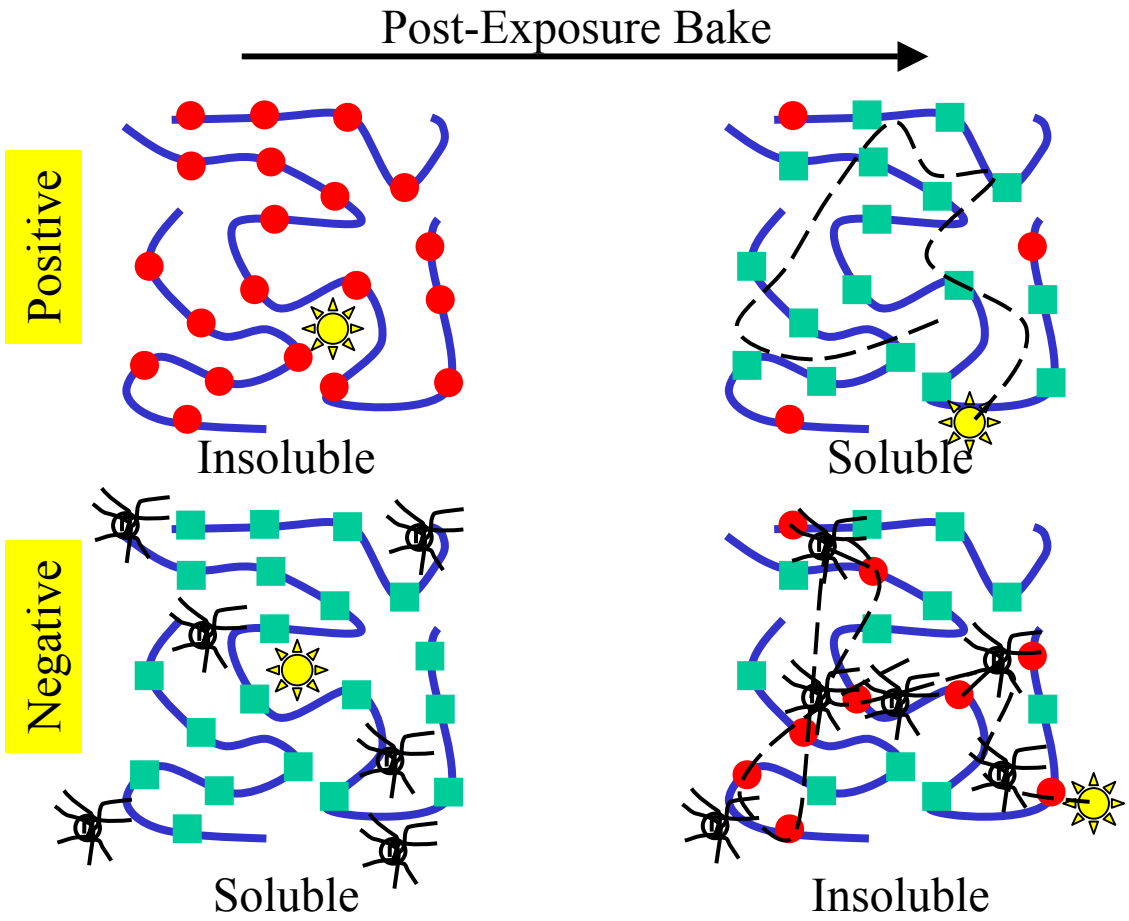
Contrast Mechanisms

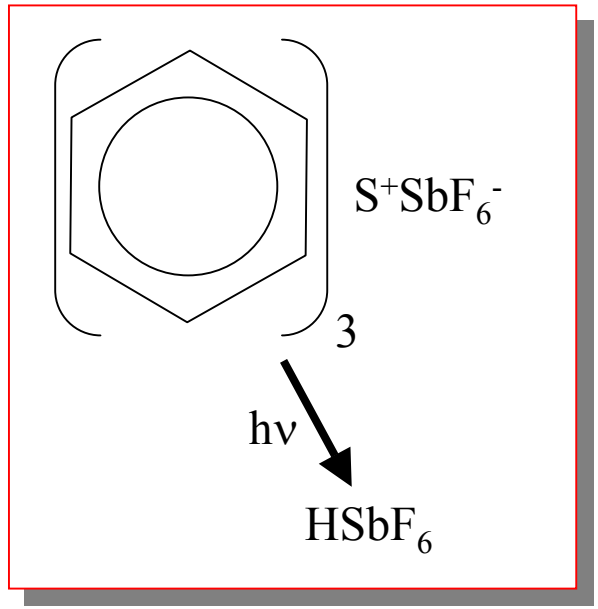
- Chemically amplified (CA) materials undergo a change in solubility *and* polarity
  - Developer attacks soluble, polar regions, affects non-polar regions much more slowly
    - Control of hydrophobicity vs hydrophilicity is critical
    - Material becomes soluble once number density of deprotected sites exceeds critical value
  - High contrast mechanism



After W.D. Hinsberg, F.A. Houle, M.I. Sanchez and G.M. Wallraff, IBM J. Res. & Dev. **45**, 667 (2001)

Chemically Amplified Resists





- Protected site
- Deprotected site
- Acid
- Cross-linker
- Backbone

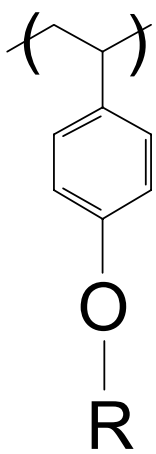
Acid Generator Properties

- Acid precursor and radiolysis products are non-volatile at maximum wafer temperature realized during wafer exposure and under conditions maintained at wafer plane
  - Acid molecules are bulky/large
  - Acid formation does not occur through a leaving reaction
  - Acid associated with polar functionalities of the resist resin component

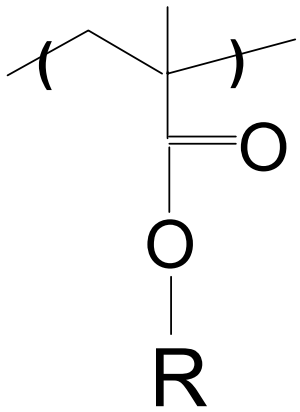
Deprotection Reaction Properties

- Kinetics (K_d) of acid catalyzed reaction zero at maximum substrate temperature ➢ high activation energy (E_a)
- Kd ≠ 0 ➢ reaction products non-volatile

a)

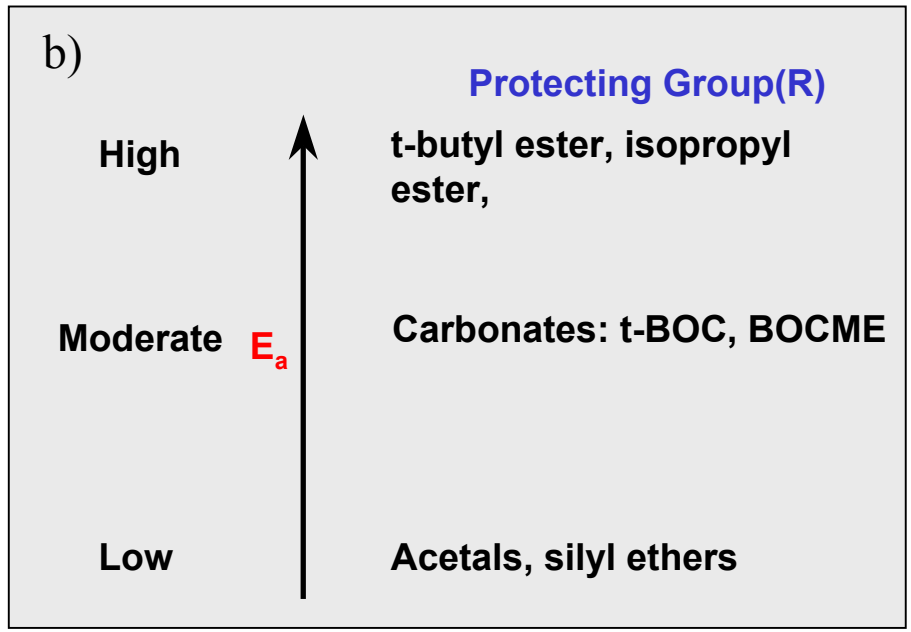


Protected hydroxystyrene
(Resin in 248 nm resists)



Protected Methacrylic Acid
(Resin in 193 nm resists)

b)



Bake Temperature & Stability

- Low E_a materials: deprotection reaction occurs at ambient temperature reducing sensitivity to PEB delay effects.
- High E_a materials: deprotection only occurs at high temperatures allowing PAB above T_g. Polymer densifies above T_g and diffusion rates of contaminants are significantly reduced.

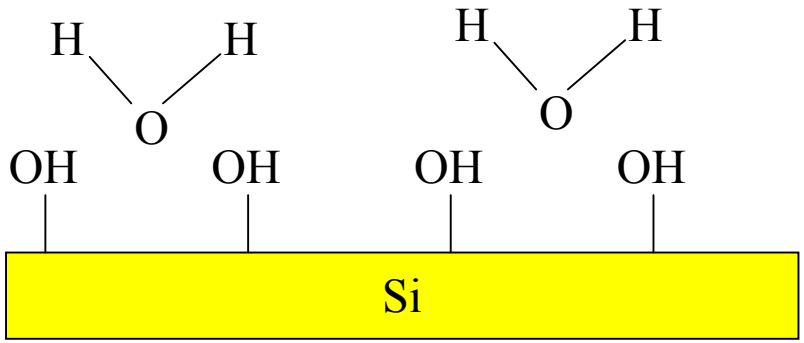
Process Stability

Process Sensitive Parameter	Value
Post-Exposure Delay (PED) Time	> 3 hrs
Development Time	< 5% CD/minute
Etch Resistance	= Polyhydroxystyrene
Post Exposure Bake (PEB)	< 1% CD/°C
Developer	0.26 N TMAH
Vacuum Compatibility	Zero outgassing

- Outgassing contaminates lithography systems – affects choice of resist chemistry
- Note optical transparency is *not* a requirement for e-beam resists

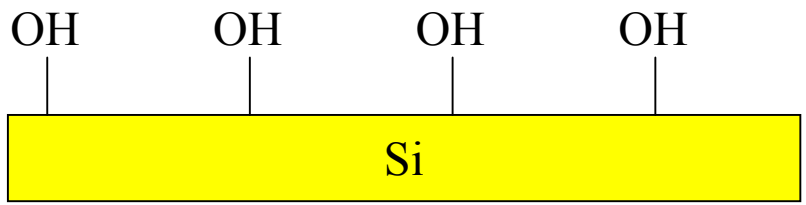
Adhesion

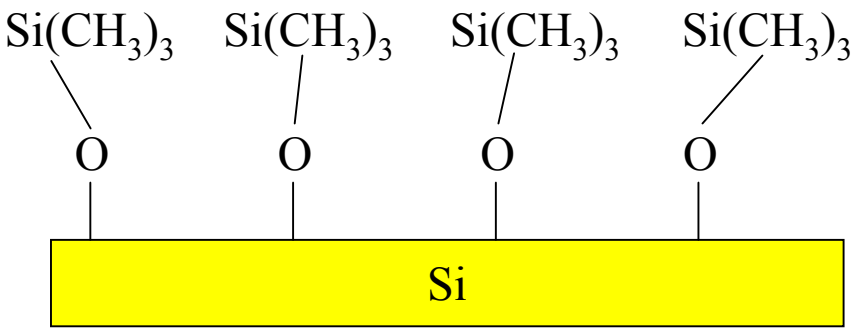
- Resist are generally non-polar and therefore do not adhere well to hydrated or polar surfaces. Termination of a surface with non-polar functionalities improves adhesion.



HMDS (Hexamethyldisilazane)

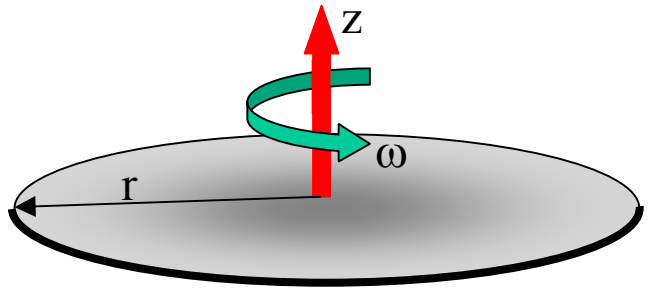
$(CH_3)_3Si\text{-}NH\text{--}Si(CH_3)_3$





Resist Coating

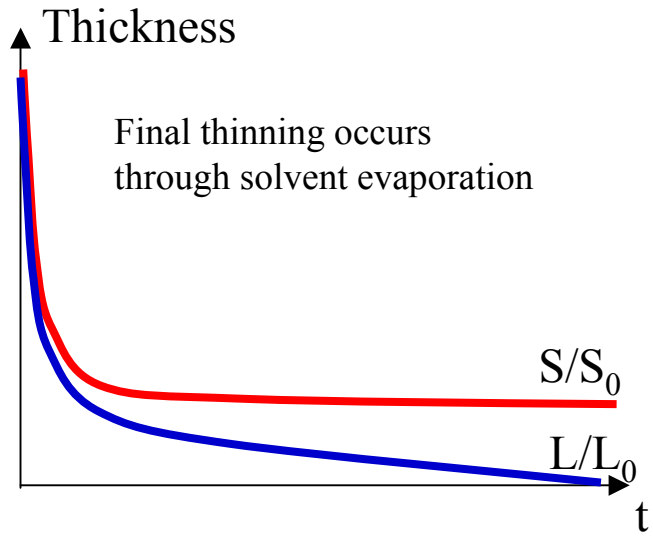
$$-\eta\frac{\partial^2 v}{\partial z^2} = \rho\omega^2 r \quad \Rightarrow Thickness \propto \frac{1}{\sqrt{\omega}}$$



Balance viscous and centrifugal forces

$\eta = viscosity,\ \rho = density,\ \omega = rotation\ rate$

Emslie, Bonner and Peck, *J. Appl. Phys.*, **29** 858 (1958)



Meyerhofer, *J. Appl. Phys.*, **49** 3993 (1978)

$$\frac{dS}{dt} = \frac{-c2\omega^2 h^3}{3\eta};\quad \frac{dL}{dt} = \frac{(1-c)2\omega^2 h^3}{3\eta} - e$$

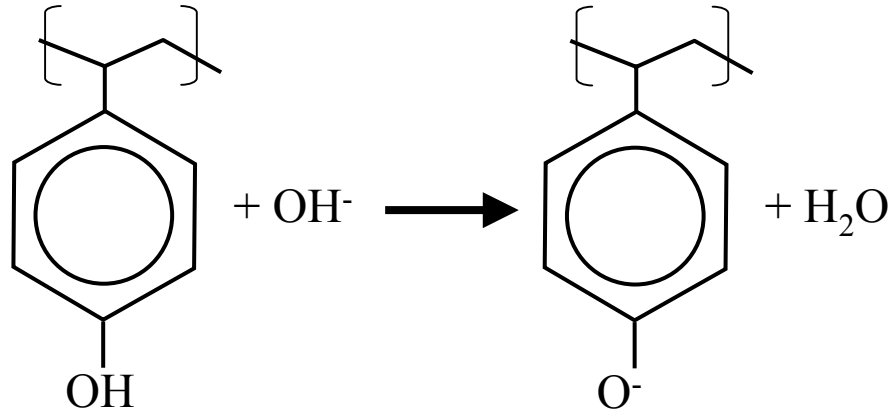
$S = solids,\ L = liquids,\ h = thickness,\ \eta = kinematic\ viscosity$

$c = solids\ concentration, e = solvent\ evaporation\ rate$

http://www.mse.arizona.edu/faculty/birnie/Coatings/FluidFlo.htm

Development

- Three main steps in dissolution:
  - Transport of OH^- ions to film surface
  - Deprotonation of phenolic group (dynamic equilibrium process)
  - Transport of ionized polymer chain into solution (depends on critical ionization fraction)



"Advancements to the critical ionization dissolution model", S.D. Burns, G.M. Schmid, P.C. Tsiartas, C. G. Willson and L. Flanagin, *J. Vac. Sci. Technol.*, **B20** p537 (2002)

"Novolak–diazonaphthoquinone resists: The central role of phenolic strings", A. Reiser, Z. Yan, Y-K. Han, and M. S. Kim, *J. Vac. Sci. Technol.*, **B18** p1288 (2000)

"Surface roughness development during photoresist dissolution", L.W. Flanagin, V.K. Singh, C. Grant Willson S.D. Burns, G.M. Schmid and P.C. Tsiartas, *J. Vac. Sci. Technol.*, **B17** p1371 (1999)

Etch Resistance

- Ability of resist to withstand physical and chemical attack during plasma etching is essential for pattern transfer.
  - Onishi parameter: $N/(N_c-N_o)$, correlates with etch rate due to energetic ion bombardment.
  - Ring parameter: M_{CR}/M_{TOT}, correlates with etch resistance in chemical etches.
  - Organosilicon materials provide good etch resistance in oxygen plasmas